Organo-Soluble Chiral Thiol-Monolayer-Protected Gold Nanorods

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Here, we report the synthesis and characterization of organo-soluble chiral thiol-monolayer-protected gold nanorods. The resulting gold nanorods respectively covered with two opposite enantiomers via the strong covalent Au−S linkage were found to not only be stable in both organic media and solid state, but also show optical activity. Their circular dichroism (CD) spectra exhibited a mirror image relationship, indicating that enantiomeric thiol surfactant on gold surface can produce the corresponding enantiomeric gold nanorods. The densely packed azobenzene thiol monolayer on gold surface exhibited a photoresponsive behavior upon irradiation with 254 nm light instead of 365 nm light, which was found to have an effect on plasmonic absorption of gold nanorods.

Introduction

The interplay between metal nanoparticle and chirality is challenging as well as fascinating for creating novel functional materials.[1−8] Among all the metal nanoparticles, gold nanorods would hold a particular promise for many applications in optics,[9−12] sensor,[13−16] imaging,[17−19] and anticancer agents[20−22] due to their unique shape-dependent optical properties. So far, gold nanorods have been mainly prepared in an aqueous solution by a seed-mediated growth method,[23−29] in which cetyltrimethylammonium bromide (CTAB) is normally used as a shape-directing surfactant. The resulting gold nanorod coated with dynamic CTAB layer is water-soluble but not stable. Compared with the hydrophilic gold nanorods, hydrophobic thiol-monolayer-protected gold nanorods possess advantages of superior stability, low interfacial energy, and good compatibility with organic media such as liquid crystals and polymers. This allows for a high degree of control during solution and surface processing as well as functionality. Interestingly, the seemingly trivial exchanging of CTAB with hydrophobic organic thiol molecules to obtain hydrophobic thiol-monolayer-protected gold nanorods was found to be difficult since the hydrophilic densely packed CTAB bilayer on its longitudinal side obstructs hydrophobic thiol molecules from accessing the gold surface to bind to the gold through a strong covalent Au−S linkage.[30,31]

It is known that gold nanoparticles may be chiral (i.e., show optical activity) if (a) the gold nanoparticle itself is chiral,[32] (b) the gold core is achiral, but the surfactants are bound onto gold surface in a chiral pattern,[33,34] or (c) the gold core itself and the binding pattern are achiral, but the surfactant is chiral.[35] However, it appears to date that the induced chirality (i.e., optical activity) in hydrophobic chiral thiol monolayer-protected gold nanorods has not been examined. Without doubt, the synthesis of optically active hybrid gold nanorods and understanding of their interaction would open the door to many applications particularly in negative index materials.[36]

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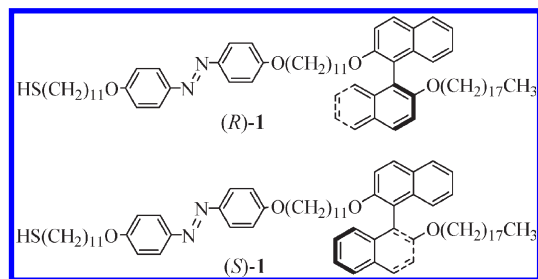| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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Figure 1. Chemical structures of axially chiral thiol surfactants (R)-(+)-**1** and (S)-(−)-**1**.
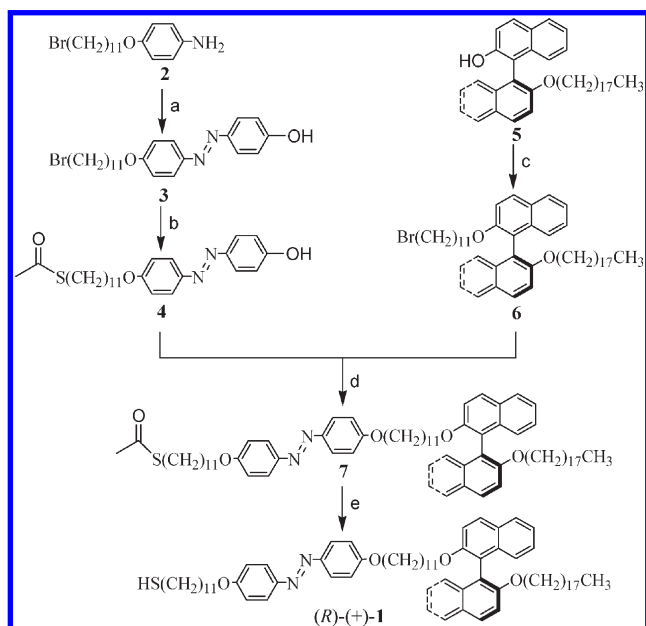

Figure 2. Synthesis of (R)-(+)-**1**. Conditions: (a) NaNO$_2$, aq. HCl, 0 °C, then phenol, NaOH, 0 °C; (b) CH$_3$COSK, acetone, room temperature; (c) 11-bromo-undecanol, PPh$_3$, diisopropyl azodicarboxylate, THF, reflux; (d) K$_2$CO$_3$, KI, acetone, reflux; (e) tetrabutylammonium cyanide, CHCl$_3$-MeOH, room temperature.

Here, we report the synthesis and characterization of organosoluble chiral thiol-monolayer-protected gold nanorods (Figure 1). The resulting gold nanorods respectively covered with two opposite enantiomers via the Au−S linkage were found to not only be stable in both organic media and solid state, but also show optical activity.

Experimental Section

Synthesis of the Chiral Thiol Surfactants (R)-(+)-1 and (S)-(−)-1. The new axially chiral azo thiol surfactant (R)-(+)-**1** was synthesized starting from (R)-(+)-1,1′-bi-(2-naphthol) (Figure 2). Its enantiomer (S)-(−)-**1** was prepared by the same procedures with (S)-(−)-1,1′-bi-(2-naphthol). Their structures were identified by ^{1}H NMR, ^{13}C NMR, FT-IR, high-resolution MS, and elemental analysis (see Supporting Information).

Data for (R)-(+)-1. ^{1}H NMR: δ 0.84−1.84 (m, 71H), 2.46−2.57 (m, 2H), 3.87−4.05 (m, 8H), 6.96−7.41 (m, 12H), 7.81−7.93 (m, 8H). ^{13}C NMR: 14.11, 22.68, 24.63, 25.59, 26.00, 28.36, 29.05, 29.13, 29.21, 29.38, 29.48, 29.71, 31.92, 34.02, 68.29, 69.76, 114.63, 115.86, 120.73, 123.34, 124.28, 125.49, 125.96, 127.73, 128.98, 129.23, 134.21, 146.94, 154.53, 161.65. IR (KBr) ν_{max} (cm^{-1}): 2922, 2853, 1601, 1460, 1248, 1149. Elemental analysis calcd for C$_{72}$H$_{102}$N$_2$O$_4$S: C, 79.22; H, 9.42; N, 2.57; S, 2.94. Found: C, 78.94; H, 9.70; N, 2.83; S, 2.94. HRMS (M+H)

calcd for C$_{72}$H$_{102}$N$_2$O$_4$SH 1091.7638; found 1091.7713. (M+Na) calcd for C$_{72}$H$_{102}$N$_2$O$_4$SNa 1113.7458, found 1113.7415.

Data for (S)-(−)-1. ^{1}H NMR: δ 0.84−1.84 (m, 71H), 2.44−2.55 (m, 2H), 3.87−4.05 (m, 8H), 6.95−7.40 (m, 12H), 7.81−7.92 (m, 8H). ^{13}C NMR: 14.11, 22.68, 24.63, 25.59, 26.00, 28.36, 29.05, 29.10, 29.13, 29.20, 29.37, 29.48, 29.71, 31.92, 34.02, 68.28, 69.75, 114.63, 115.86, 120.72, 123.34, 124.28, 125.49, 125.97, 127.73, 128.98, 129.23, 134.21, 146.93, 154.53, 161.14. HRMS (M+H) calcd for C$_{72}$H$_{102}$N$_2$O$_4$SH: 1091.7638; found 1091.7713. (M+Na) calcd for C$_{72}$H$_{102}$N$_2$O$_4$SNa 1113.7458, found 1113.7472.

Preparation of CTAB Bilayer Coated Gold Nanorods. The CTAB bilayer coated gold nanorods were freshly prepared by the seed-mediated growth method.[27] For seed preparation, specifically, 0.50 mL of an aqueous 0.01 M solution of HAuCl$_4$ was added to 15 mL of a 0.10 M CTAB solution in a vial. The solutions were gently mixed by the inversion. The solution appeared a bright brown-yellow color. Then, 1.20 mL of an aqueous 0.01 M ice-cold NaBH$_4$ solution was added all at once, followed by rapid inversion mixing for 2 min. Care should be taken to allow the escape of evolved gas during mixing. The solution developed a pale brown-yellow color. Then, the vial was kept in a water bath maintained at 25 °C for future use. This seed solution was used 2 h after its preparation and could be used over a period of 1 week.

4.75 mL of 0.1 M CTAB solution in water was added to a tube, then 0.20 mL of 0.01 M solution of HAuCl$_4$ and 0.03 mL of 0.01 M AgNO$_3$ were added in this order and mixed by inversion. Then, 0.03 mL of 0.1 M of ascorbic acid solution was added and the resulting mixture at this stage becomes colorless. 0.01 mL of the seed solution was added to the above mixture tube, and the tube was slowly mixed for 10 s and left to sit still in the water bath at 25−30 °C for 3 h. The final solution turned purple within minutes after the tube was left undistubed.

Synthesis of Organo-Soluble Thiol-Monolayer-Protected Gold Nanorods. The solution of CTAB coated gold nanorods was centrifuged several times to remove the excessive CTAB and other solution components and redispersed in 2 mL of water. Then, this aqueous solution of gold nanorods was added dropwise to a solution of the thiol surfactant (100 mg) in 50 mL of dry THF with stirring under the protection of nitrogen. The color of the reaction mixture is purple. The reaction mixture was continued to stir at room temperature for 3 days. The mixture was evaporated to dryness under reduced pressure. CH$_2$Cl$_2$ was added to dissolve the nanorods followed by centrifuging several times to remove excess thiol and CTAB (at 12 000 rpm, 16 min). The resulting gold nanorods were redispersed in CH$_2$Cl$_2$ with addition of excess thiol surfactant and stirred for another 24 h and centrifuged. This procedure was repeated three times to ensure that the gold nanorods were encapsulated with the thiol molecules over the entire surface through the strong covalent Au−S linkage. The as-prepared chiral hybrid gold nanorods were centrifuged and washed with CH$_2$Cl$_2$ several times until there was no UV, IR, or CD absorption in the top layer solution, i.e., there is no free thiol in the thiol-monolayer-protected gold nanorods. The thiol-monolayer-protected gold nanorods are very stable in both organic media and the solid state.

I$_2$ Induced Decomposition of Hybrid Gold Nanorods. In a typical procedure, ca. 10 mg hybrid gold nanorods were dissolved in CDCl$_3$ and the ^{1}H NMR spectrum was collected. Then, 1 mg iodine was added to this solution and followed by stirring at room temperature for 3 h. The decomposition process could be monitored by a change in solution color from dark brown to clear purple. After removal of bulk gold by centrifuging, the top layer clear solution was evaporated and the ^{1}H NMR spectrum was collected for comparison with the spectrum before decomposition.

Results and Discussion

The CTAB bilayer coated gold nanorods were prepared by the seed-mediated growth method[27] in deionized water. After removal of most CTAB by centrifuging, the water-soluble gold
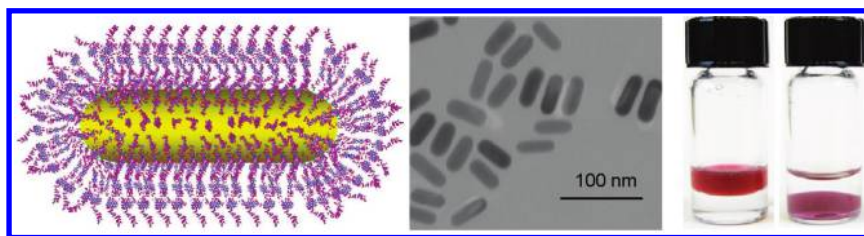
Figure 3. Left: Schematic representation of chiral thiol (*R*)-(+)-**1** monolayer-protected gold nanorod. Middle: TEM image of (*R*)-(+)-**1** thiol monolayer-protected gold nanorods. Right: Photograph of CTAB bilayer coated gold nanorods (left) and (*R*)-(+)-**1** thiol monolayer-protected gold nanorods (right) (top layer, water; bottom layer, CH_2Cl_2).
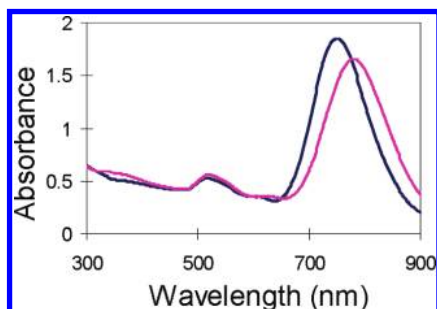

Figure 4. UV−vis-NIR spectra of CTAB bilayer coated gold nanorods (blue) and (*R*)-(+)-**1** thiol-monolayer-protected gold nanorods (pink).

nanorods were treated with thiol surfactant in THF at room temperature for 3 days followed by centrifuging and further exchange with thiol for 24 h. After this process was repeated 3 times, the chiral thiol-monolayer-protected gold nanorods were centrifuged and washed with CH_2Cl_2 several times until there was no UV, IR, or CD absorption in the top layer solution, i.e., there is no free thiol in the thiol-monolayer-protected gold nanorods. The resulting thiol-monolayer-protected gold nanorods remained stable in CH_2Cl_2 without any aggregation even after several months, and they can be easily redispersed in CH_2Cl_2 after removal of solvents. Nonaggregated gold nanorods in organic solvent were evidenced by transmission electron microscopy (TEM) observation (Figure 3 middle) with the average size 50 nm × 17 nm and aspect ratio 3:1 approximately. As expected, they are very soluble in organic solvents.

UV−vis-NIR spectra of CTAB bilayer coated and thiol-monolayer-protected gold nanorods (Figure 4) exhibited the two characteristic plasmon bands of gold nanorods: a strong longitudinal band in the near-infrared region corresponding to the electron oscillation along the long axis and a weak transverse band, similar to that of gold nanospheres, in the visible region corresponding to electron oscillations along the short axis. The slightly red-shifted spectrum of thiol-monolayer-protected gold nanorods compared with CTAB coated rods can possibly be due to size selection in the centrifugation steps or a change in the resonance due to the different dielectric properties of the thiol protecting layer. Infrared (IR) spectrum of the thiol-monolayer-protected gold nanorods exhibited the characteristic ether linkage at 1240 cm^{-1}, which is similar to that of free thiol surfactant (Figure 5). This further confirms the binding of the thiol surfactants to the gold surface.

Figure 6 shows the Raman spectrum, showing a characteristic Au−Br band at 180 cm^{-1} and CH_2 band at 760 cm^{-1} for CTAB
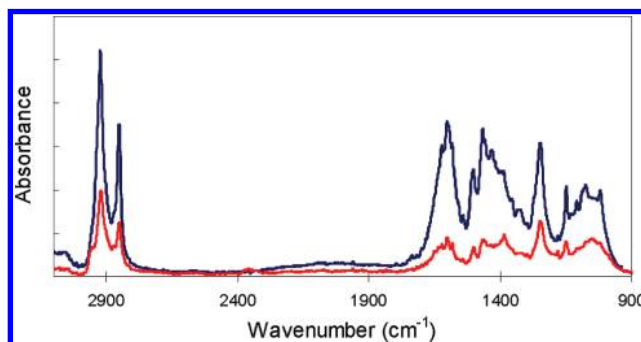

Figure 5. IR spectra of free thiol surfactant (*R*)-(+)-**1** (blue) and its thiol-monolayer-protected gold nanorods (red).
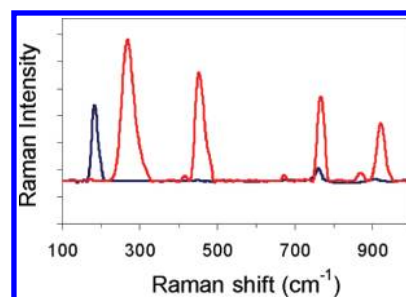

Figure 6. Raman spectra of the CTAB bilayer coated gold nanorods (blue) and (*R*)-(+)-**1** thiol monolayer-protected gold nanorods (red).

bilayer coated gold nanorods.[37,38] As expected, the characteristic Au−Br band disappeared in the Raman spectrum of the thiol-monolayer-protected gold nanorods, accompanied with the appearance of new Raman peaks especially the Au−S bond around 260 cm^{-1}.[39] This provides clear evidence that no CTAB remained in the thiol-monolayer-protected gold nanorods, and the thiol molecules had been successfully bound onto the gold surface.

Interestingly, compared to the ^{1}H NMR spectrum of the free thiol surfactant, many peaks of the thiol-monolayer-protected gold nanorods disappeared except some broaden peaks at high field (Figure 7, top), which is different from the previously reported significant peak broadening phenomenon in ^{1}H NMR of the thiol monolayer-protected spherical gold nanoparticles.[40−43] The significant peak broadening phenomenon in ^{1}H NMR of monolayer-protected gold nanoparticles might result from three main causes: (a) the tight packing of protons close to the Au core causes rapid spin−spin relaxation from dipolar interactions;

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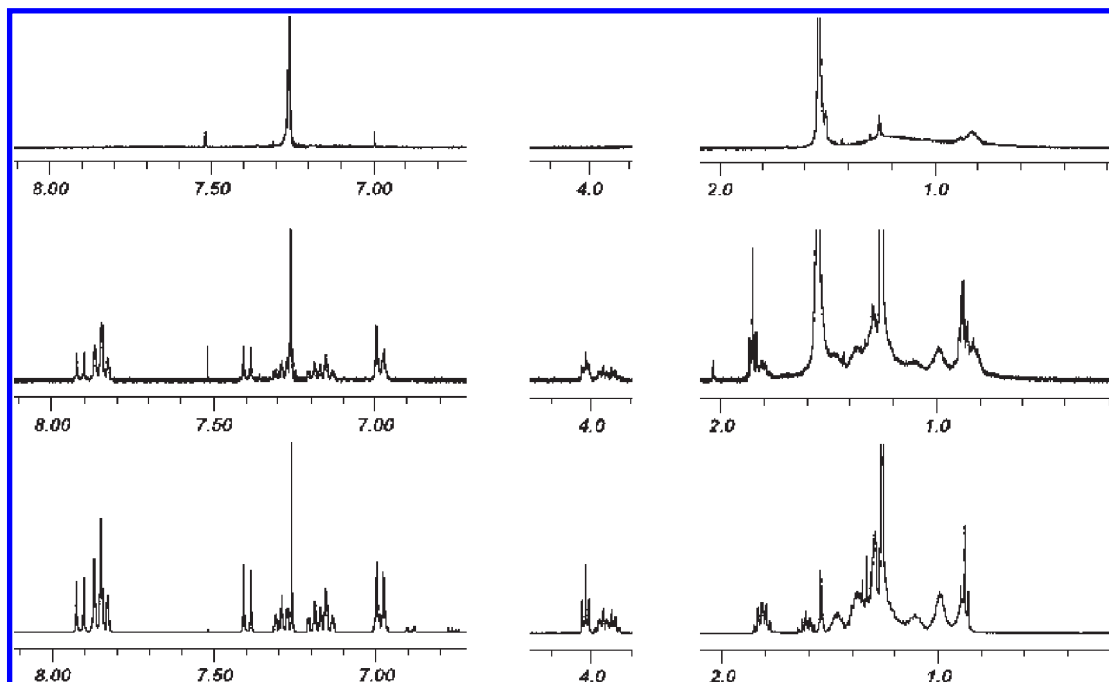
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Figure 7. ^{1}H NMR of (R)-(+)-**1** monolayer-protected gold nanorods (top), the hybrid gold nanorods after I$_2$ induced decomposition (middle), and the free thiol surfactant (R)-(+)-**1** (bottom).
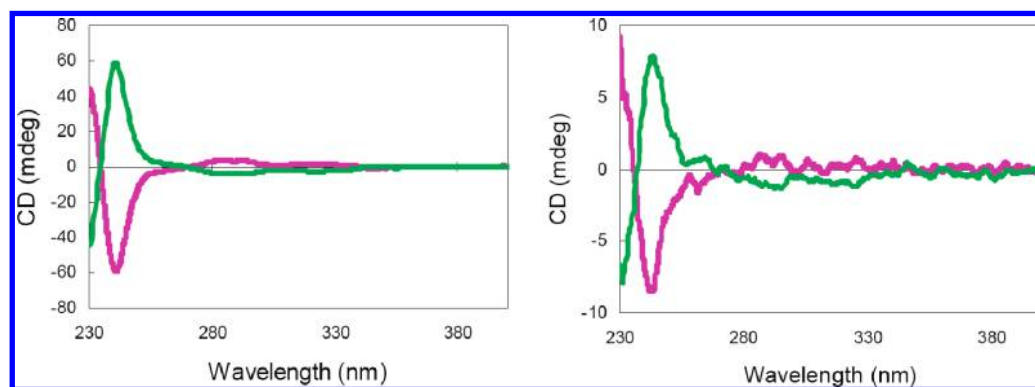

Figure 8. Left: CD spectra of chiral thiol (R)-(+)-**1** (pink) and (S)-(−)-**1** (green) in CH$_2$Cl$_2$. Right: CD spectra of (R)-(+)-**1** monolayer-protected gold nanorods (pink) and (S)-(−)-**1** monolayer-protected gold nanorods (green) in CH$_2$Cl$_2$.

(b) there are different binding sites on the Au core surface and the chemical shift differences also vary with core size and structure; (c) the size-dependent rotation diffusion of the clusters leads to size-dependent spin−spin relaxation broadening, which means the peak is getting broad with the increase in size. The gold nanorods studied here have relatively large size, and surfactants on their surface are more densely packed and solid-like (especially on the longitudinal side of gold nanorods where the surfactants are packed like self-assembled monolayers) and thereby experienced much faster spin−spin relaxation compared with those of gold nanoparticles; as a result, the peak became much broader and nearly flat. The upfield peaks are related to the relatively mobile alkyl chain ends of the surfactant. To further check this point, we used the iodine decomposition method[44] to decompose thiol-monolayer-protected gold nanorods. After the removal of bulk gold, the top layer organic solution was evaporated and its ^{1}H NMR data collected (Figure 7, middle). As expected, most of the disappeared peaks reappeared, similar to that of free thiol

(Figure 6, bottom). The ^{1}H NMR data also confirmed that the thiol surfactant was bound onto the gold surface through the successful exchange with the surface-coated CTAB moieties.

The optical activity of (R)-(+)-**1** thiol monolayer-protected gold nanorods and (S)-(−)-**1** thiol monolayer-protected gold nanorods were characterized by CD spectra shown in Figure 8 (right). Their CD spectra exhibited a mirror image relationship with a strong sharp peak at about 240 nm which means that an enantiomeric thiol surfactant on gold surface can produce the corresponding enantiomeric gold nanorods. However, no CD signal was observed in not only their top clear solution after centrifuging, but also the water-soluble CTAB bilayer coated gold nanorods. This clearly indicated that both (R)-(+)-**1** thiol-monolayer-protected gold nanorods and (S)-(−)-**1** thiol-monolayer-protected gold nanorods are optically active. Interestingly, their CD spectra are quite similar to the spectra of free thiol surfactant (Figure 8, left). It might be attributed to the fact that the induced optical activity in gold nanoparticles originating from the vicinal effect was size-dependent,[4,34] i.e., a decrease in induced optical activity with an increase in cluster size. Since the gold nanorods have much larger size than spherical gold nanoparticles

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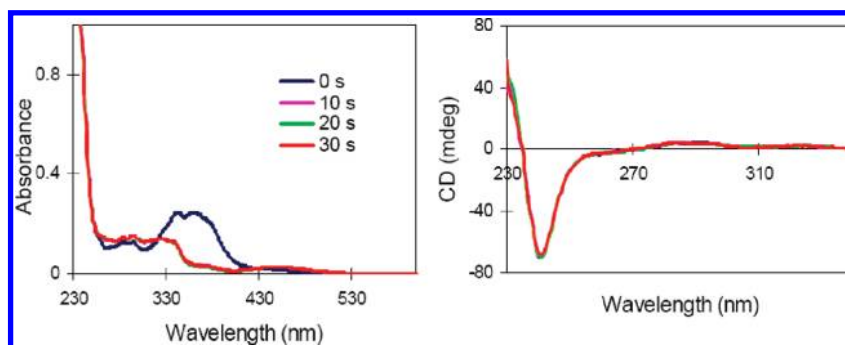
Figure 9. UV−vis (left) and CD (right) spectra of thiol (*R*)-(+)-**1** solution in CH$_2$Cl$_2$ upon UV irradiation at 365 nm for 0 s (blue), 10 s (pink), 20 s (green), and 30 s (red).
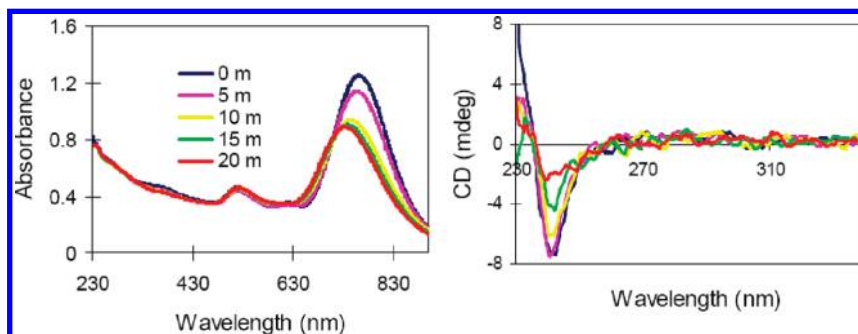

Figure 10. UV−vis-NIR (left) and CD (right) spectra of (*R*)-(+)-**1** monolayer-protected gold nanorods under UV irradiation at 254 nm for 0 min (blue), 5 min (pink), 10 min (yellow), 15 min (green), and 20 min (red).
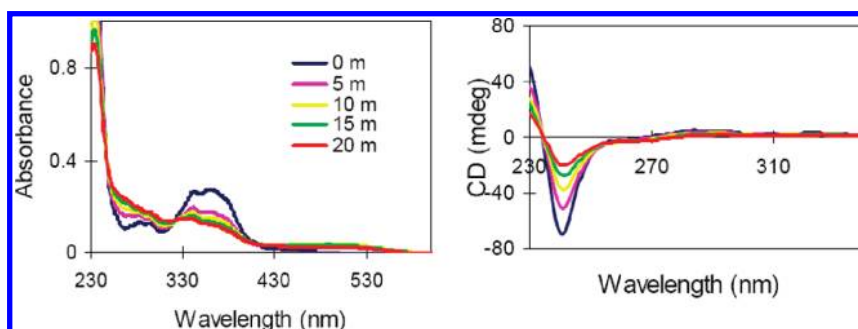

Figure 11. UV−vis (left) and CD (right) spectra of (*R*)-(+)-**1** under UV irradiation at 254 nm for 0 min (blue), 5 min (pink), 10 min (yellow), 15 min (green), and 20 min (red).

(diameter < ∼3 nm), obviously the vicinal effect is less possible. Furthermore, the chiral moiety of the thiol surfactants is far away from the surface of gold nanorod (> 20 carbons). As a result, the chiral moiety might have less effect on the electron transitions of the gold cores.[8]

The two azo thiol surfactants exhibited the expected photoresponsive behavior. For example, (*R*)-(+)-**1** underwent a fast photoisomerization (ca. 10 s) from the trans to the cis conformation in CH$_2$Cl$_2$ upon irradiation with 365 nm light, evidenced by UV−vis spectra change. Interestingly, its CD spectra remained unchanged in this process (Figure 9). However, when the hybrid gold nanorod solutions were exposed to UV light at 365 nm, no obvious photoresponsive behavior was observed in both UV and CD spectra even with a relatively long irradiation time (10 min). The reason could be that the azobenzene cores are densely packed

on a gold surface in a similar manner to self-assembled monolayers (SAMs); thus, the photoisomerization is sterically hindered.[45−47] Surprisingly, when the solution of hybrid gold nanorods was irradiated with 254 nm light, the longitudinal band in its UV−vis-NIR spectra was found to experience a blue shift and decrease in intensity, and its CD signal showed a tendency to decrease in intensity (Figure 10). It is worth noting here that the gold nanorod solution remained clear, and no aggregation was observed during this process and even after several days, indicating that the surfactant was still bound on the gold surface. Also, the heat effect derived from UV light can be ruled out, since no UV−vis-NIR and CD spectra changes were observed when the solution of gold nanorods was heated at 40 °C for 10 min. A similar intensity decrease was observed in CD spectra of (*R*)-(+)-**1** solution upon irradiation at 254 nm, and its UV−vis spectra also showed a slow isomerization from trans to cis form (Figure 11). Undoubtedly, the CD spectra changes are not related to the

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isomerization process evidenced by no CD changes being found in fast isomerization upon irradiation at 365 nm. These results showed that the surfactant on a gold surface might experience photoracemization upon long-term irradiation at 254 nm, which caused the decrease of CD intensity.[48−50] However, this mechanism remains unclear. Further research is underway.

Conclusion

In conclusion, gold nanorods respectively encapsulated with the two opposite chiral azo thiol enantiomers over the entire surface via the strong covalent Au−S linkage were, for the first time, synthesized and characterized. The resulting organo-soluble gold nanorods were found to not only be very stable in both organic media and solid state, but also show optical activity. The densely packed azobenzene thiol monolayer on gold surface exhibited a photoresponsive behavior upon irradiation with 254 nm light instead of 365 nm light, which was found to have an effect on plasmonic absorption of gold nanorods. The concept demonstrated here provides new insight into tailoring the structure of chiral hybrid gold nanorods with properties of practical significance by using functional chiral thiol surfactants.

Supporting Information Available: Details of surfactant synthesis, the procedure for large scale synthesis of hybrid gold nanorods, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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